Journal of Solid State Chemistry **159**, 59–67 (2001)
doi:10.1006/jssc.2001.9130, available online at http://www.idealibrary.com on IDEAL®

Synthesis and Characterization of an Organically Templated Lamellar Vanadium–Gallium Phosphate, $[NH_3(CH_2)_2NH_3]_4[Ga_{4-x}V_x(HPO_4)_5(PO_4)_3H(OH)_2] (x = 1.65)$

Ann M. Chippindale*,[1] and Andrew R. Cowley†

Department of Chemistry, The University of Reading, Whiteknights, Reading, Berks RG6 6AD, U.K.; and †Chemical Crystallography Laboratory, University of Oxford, 9 Parks Road, Oxford OX1 3PD, U.K.

Received October 13, 2000; in revised form January 26, 2001; accepted February 15, 2001;

A new two-dimensional vanadium–gallium phosphate (VGaPO), $[NH_3(CH_2)_2NH_3]_4[Ga_{4-x}V_x(HPO_4)_5(PO_4)_3H(OH)_2]$ ($x = 1.65$), has been synthesized under solvothermal conditions at 433 K in the presence of ethylenediamine and the structure determined using room-temperature single-crystal X-ray diffraction data ($M_r = 1296.22$, triclinic, space group $P-1$; $a = 9.991(1)$, $b = 12.367(1)$, and $c = 15.082(1)$ Å; $\alpha = 90.751(6)$, $\beta = 91.720(7)$, and $\gamma = 91.449(8)°$; $V = 1861.8.4$ Å^3; $Z = 2$; $R = 3.93\%$ and $R_w = 4.77\%$ for 5985 observed data ($I > 3(\sigma(I))$). The inorganic layers consist of PO_4 tetrahedra and M_4O_{20} ($M = V$, Ga) tetramers assembled from edge- and corner-sharing MO_6 octahedra. The structure contains various types of hydrogen bonding interactions: short symmetrical and asymmetrical hydrogen bonds within the layers, strong interlamellar hydrogen bonds holding the layers together, and amine-framework interactions holding the ethylenediammonium cations in place in the interlayer voids. © 2001 Academic Press

Key Words: **solvothermal synthesis; crystal structure; single-crystal XRD; MeGaPO; vanadium–gallium phosphate; organically templated; layer structure; open-framework structure.**

INTRODUCTION

A number of open-framework heterometal-substituted gallium phosphates (*Me*GaPOs) have been synthesized under mild solvothermal conditions using organic amines or diamines as structure-directing agents (1, 2). Many examples are now known incorporating the first-row transition metals Mn, Fe, Co, and Zn as divalent cations which, as well as being interesting for their potential catalytic activities, exhibit a rich structural chemistry. Both zeolite analogues and new 3-D structure types assembled from alternately linked MO_4 and PO_4 tetrahedral units have been reported. For example, $[TH][MeGa_2(PO_4)_3]$ (Me = Mn, Fe, Co, Zn; T = pyridine (C_5H_5N), imidazole ($C_3H_4N_2$) (3, 4), $[TH][MeGa(PO_4)_2]$ (Me = Co, Zn; T = pyrrolidine (C_4H_9N)) (5, 6), and $[T][ZnGa_2(PO_4)_3]$ (T = tetramethylammonium ($(CH_3)_4N$)) (7) are isostructural with the zeolites laumontite, gismondine, and sodalite, respectively, whereas $[TH_2]_2[Me_4Ga_5(PO_4)_9]$ (Me = Co, Zn; T = DABCO ($C_6H_{12}N_2$)) (2, 8), $[TH][MeGa_3(PO_4)_4]$ (Me = Co, Zn; T = quinuclidine ($C_7H_{13}N$)) (2, 9), and the series UCSB-6, -8 and -10 (10) have new structure types. The metal species in *Me*GaPOs are not, however, restricted solely to tetrahedral coordination. Thus, $[NH_4][MeGa_2(PO_4)_3(H_2O)_2]$ (Me = Mn, Fe, Co, Zn) (11, 12) contains MeO_6 octahedra and GaO_5 trigonal bipyramids and $[TH_2][MnGa(HPO_4)_2(PO_4)]$ (T = DABCO ($C_6H_{12}N_2$)) (13) has MnO_5 square pyramids together with GaO_4 tetrahedra. More recently, a mixed-valence MnGaPO, $[TH_2]_2[Mn_2Ga_5(PO_4)_8(H_2O)]$ (T = piperazine ($C_4H_{10}N_2$)) (14), has been prepared in which there are edge-sharing GaO_6 octahedra in Ga_2O_{10} units, GaO_5 trigonal bipyramids with $Mn^{II}O_4$, and $Mn^{III}O_4$ tetrahedra.

To date, only two examples are known of amine-templated gallium phosphate phases incorporating vanadium. The vanadium is trivalent in both of these VGaPOs. The first example, $[NH_3(CH_2)_4NH_3]_2[Ga_{3.6}V_{0.4}(HPO_4)_2(PO_4)_3(OH)_3]$. yH_2O ($y \sim 5.4$) (15), has a 3-D framework structure assembled from PO_4 tetrahedra and M_4O_{20} (M = V, Ga) tetrameric units. The latter, "secondary building blocks," consist of a central pair of edge-sharing MO_6 octahedra connected by corner sharing at the hydroxo oxygens of the common edge to two additional MO_6 units. A 3-D network of tunnels bounded by 20-ring windows of alternating MO_6 and PO_4 polyhedra runs through the structure accommodating the diprotonated amine and water molecules. In the second phase, $[NH_3(CH_2)_2NH_3][Ga_{0.35}V_{0.65}(H_2PO_4)(P_2O_7)]$ (16), isolated MO_6 octahedra are linked through PO_4 and P_2O_7 units to form a 1-D chain structure. Ethylenediamine dications are located in the interchain voids. A network of hydrogen

---

[1] To whom correspondence should be addressed. E-mail:a.m.chippindale@rdg.ac.uk.

bonds involving both interchain and chain–diamine interactions serves to hold the structure together. A third vanadium–gallium phosphate framework has also been prepared under hydrothermal conditions using alkali-metal cations as the charge-balancing species. In $A[(VO)Ga(PO_4)_2(H_2O)]$ ($A = Rb$, Cs) (17), the 3-D VGaPO framework is constructed from PO_4 and GaO_4 tetrahedra and $VO_5(H_2O)$ octahedra, in which the vanadium is present as V^{4+}.

In the present work, we report the synthesis and characterization of $[NH_3(CH_2)_2NH_3]_4[Ga_{4-x}V_x(HPO_4)_5(PO_4)_3H(OH)_2]$ ($x = 1.65$), a new two-dimensional vanadium–gallium phosphate made in the presence of ethylenediamine in which both V^{3+} and Ga^{3+} are present in octahedral coordination. To our knowledge, this is the first layered *Me*GaPO to be prepared.

EXPERIMENTAL

Synthesis and Initial Characterization

Single crystals of the title compound, $[NH_3(CH_2)_2NH_3]_4[Ga_{4-x}V_x(HPO_4)_5(PO_4)_3H(OH)_2]$ ($x = 1.65$), were prepared under solvothemal conditions (reaction (i), Table 1). Ga_2O_3 (0.237 g) and V_2O_5 (0.250 g) were dispersed in a mixture of ethylene glycol (5.6 cm^3) and water (0.69 cm^3) by stirring followed by addition of ethylenediamine (0.76 cm^3) and a small amount of the mineralizer $Si(OEt)_4$ (18). Aqueous H_3PO_4 (1.37 cm^3, 85% by weight) was then added and the gel stirred until homogenous, sealed in a Teflon-lined stainless-steel autoclave, and heated at 433 K for 7 days. The solid product was collected by filtration, washed with water, and left to dry in air at 343 K.

The product of reaction (i) consisted of a mid-green polycrystalline powder containing thin dark-green plates of edge lengths ca. 0.2–0.4 mm. The latter were studied by single-crystal X-ray diffraction as described below and found to have the composition $[NH_3(CH_2)_2NH_3]_4[Ga_{4-x}V_x(HPO_4)_5(PO_4)_3H(OH)_2]$ ($x = 1.65$). A powder X-ray diffraction pattern was recorded for a ground sample of the bulk product of reaction (i) using a Philips PW1710 diffractometer (graphite-monochromated Cu*K*α radiation ($\lambda_1 = 1.5406$ Å, $\lambda_2 = 1.5444$ Å)). All peaks in the powder pattern (Table 2) can be indexed on the basis of the triclinic cell derived from the single-crystal study with refined lattice parameters: $a = 9.998(3)$, $b = 12.371(3)$, and $c = 15.0876(3)$ Å; $\alpha = 90.750(1)$, $\beta = 91.72(2)$, and $\gamma = 91.450(1)°$. Energy-dispersive X-ray and combustion analyses further confirmed that the sample was monophasic. The former technique, performed on a finely ground sample using a JEOL 2000FX analytical electron microscope with α-$GaPO_4$ (19) and α-$VOPO_4 \cdot 2H_2O$ (20) as calibration standards, showed that each crystallite examined contained Ga, V, and P, but no Si. The P:(Ga + V) ratio of 2.10(4) and the mean composition of $Ga_{2.31(6)}V_{1.66(6)}P_8O_z$ (oxygen content cannot be determined by this technique) are in good agreement with the corresponding values obtained from the single-crystal studies. Combustion analysis gave the following results, C, 7.48; H, 3.96; N, 8.60%, which compare well with the values calculated for the proposed formula $[NH_3(CH_2)_2NH_3]_4[Ga_{4-x}V_x(HPO_4)_5(PO_4)_3H(OH)_2]$ ($x = 1.65$), C, 7.41; H, 3.74; N, 8.64%. Given the mid-green color of the products, it is likely that the vanadium is present as V^{3+}. Reduction of V^{5+} to V^{3+} in the presence of an organic amine has been reported previously in the formation of $[NH_3(CH_2)_4NH_3]_2[Ga_{3.6}V_{0.4}(HPO_4)_2(PO_4)_3(OH)_3]$. $6H_2O$ from V_2O_5, Ga_2O_3, H_3PO_4, and 1,4-diaminobutane (15).

Thermogravimetric analysis was performed using a Stanton Redcroft STA 1500 thermal analyzer over the temperature range 293–873 K at a heating rate of 5 K min^{-1} under flowing nitrogen. The sample lost weight gradually over the range 523–773 K with a total weight loss of ~ 22.2%. Assuming a mean composition of $[NH_3(CH_2)_2NH_3]_4[Ga_{4-x}V_x(HPO_4)_5(PO_4)_3H(OH)_2]$ ($x = 1.65$), the loss of four ethylenediamine and either two or three water

TABLE 1
Summary of Gel Compositions and Reaction Products

Reaction	Gel composition	Products
(i)	0.101 V_2O_5 : 0.093 Ga_2O_3 : 1.47 H_3PO_4 : 52.0 H_2O : 0.1 $Si(OEt)_4$: 1.00 $NH_2(CH_2)_2NH_2$	Sole product: $[NH_3(CH_2)_2NH_3]_4[Ga_{4-x}V_x(HPO_4)_5(PO_4)_3H(OH)_2]$ ($x = 1.65$) (powder and single crystals)
(ii)	0.194 Ga_2O_3 : 1.47 H_3PO_4 : 52.0 H_2O : 0.1 $Si(OEt)_4$: 1.00 $NH_2(CH_2)_2NH_2$	Major products: $[NH_3(CH_2)_2NH_3][Ga(H_2PO_4)(P_2O_7)]$ (powder) (16), α-$GaPO_4$ (single crystals), and $[NH_3(CH_2)_2NH_3][Ga_2(HPO_4)_2(PO_4)_2]$ (powder) (21)
(iii)	0.194 V_2O_5 : 1.47 H_3PO_4 : 52.0 H_2O : 0.1 $Si(OEt)_4$: 1.00 $NH_2(CH_2)_2NH_2$	Unidentified poorly crystalline green powder

TABLE 2
Powder X-Ray Diffraction Data for $[NH_3(CH_2)_2NH_3]_4[Ga_{4-x}V_x(HPO_4)_5(PO_4)_3H(OH)_2]$ ($x = 1.65$)

Relative intensity	$2\theta_{obs}$/deg	d_{obs}/Å	d_{calc}/Å	h	k	l
7	9.175	9.630	9.628	0	− 1	1
100	9.310	9.491	9.498	0	1	1
8	10.430	8.474	8.447	− 1	0	1
5	10.745	8.227	8.214	1	0	1
5	11.195	7.897	7.871	1	− 1	0
4	11.505	7.685	7.675	1	1	0
3	12.725	6.951	6.934	1	− 1	1
1	16.115	5.495	5.486	− 1	1	2
1	16.725	5.296	5.294	1	1	2
1	17.750	4.993	4.995	2	0	0
1	18.515	4.788	4.785	− 2	0	1
2	20.360	4.358	4.355	− 1	2	2
2	20.815	4.264	4.265	− 1	1	3
5	22.230	3.995	3.990	0	3	− 1
2	23.050	3.855	3.845	1	− 3	0
9	23.550	3.774	3.776	1	− 3	0
1	24.370	3.649	3.646	1	− 2	3
5	25.355	3.510	3.511	− 2	2	2
5	26.370	3.377	3.377	2	2	2
2	26.705	3.335	3.335	2	1	3
3	27.495	3.241	3.239	0	− 2	4
9	27.885	3.197	3.199	0	2	4
21	28.210	3.161	3.166	0	3	3
7	28.830	3.094	3.092	− 1	− 2	4
5	30.060	2.970	2.971	− 2	3	2
7	30.615	2.918	2.919	− 3	2	1
7	31.185	2.866	2.866	− 3	− 2	1
1	31.720	2.818	2.816	− 3	0	3
2	32.655	2.740	2.739	3	− 2	2
2	33.000	2.712	2.713	1	4	2
2	33.295	2.689	2.690	3	− 1	3
3	34.084	2.628	2.628	− 1	2	5
2	34.795	2.576	2.576	− 3	2	3
3	36.865	2.436	2.437	2	4	2
4	37.190	2.416	2.415	1	− 5	0

Note. Refined triclinic lattice parameters at 293 K ($0 \leq 2\theta \leq 40°$): $a = 9.998(3)$, $b = 12.371(3)$, and $c = 15.0876(3)$ Å; $\alpha = 90.750(1)$, $\beta = 91.72(2)$, and $\gamma = 91.450(1)°$ (Cu$K\alpha_1$ radiation, $\lambda = 1.5406$ Å).

molecules would correspond to weight losses of 21.33 and 22.72%, respectively. The final product was black and X-ray amorphous.

Attempts were made to prepare the Ga- and V-only analogues of this new mixed-metal phase. The synthetic procedure described above was again used with the same quantites of phosphoric acid, water, and organic components (Table 1). However, the amounts of Ga_2O_3 and V_2O_5 were adjusted to 0.495 g and 0.480 g for reactions (ii) and (iii), respectively, to keep the metal:phosphorus ratio the same as for reaction (i).

The product of reaction (ii) consisted of a mixture of products: colorless faceted blocks of α-$GaPO_4$ identified from unit-cell determination by single-crystal X-ray diffraction (19) and a white polycrystalline powder containing the phosphate-diphosphate $[NH_3(CH_2)_2NH_3]$ $[Ga(H_2PO_4)(P_2O_7)]$ (monoclinic, space group Cc; $a = 8.619(1)$, $b = 14.956(2)$, $c = 9.476(1)$ Å; and $\beta = 106.855(7)°$) (16) and a new phase, $[NH_3(CH_2)_2NH_3][Ga_2(HPO_4)_2(PO_4)_2]$ (triclinic, space group $P-1$; $a = 8.288(1)$, $b = 8.634(1)$, and $c = 14.513(2)$ Å; and $\alpha = 89.429(8)$, $\beta = 83.206(8)$, and $\gamma = 70.592(7)$ °). The structure of the latter will be reported elsewhere (21). Reaction (iii) produced a glassy, green solid which was X-ray amorphous.

There was no evidence from the powder X-ray patterns of products (ii) or (iii) for the presence of the gallium or vanadium analogues of the title compound.

Single-Crystal X-Ray Diffraction

A dark-green single crystal of the title compound in the form of a thin plate from the product of reaction (i) was mounted on a thin glass fiber using cyanoacrylate adhesive. X-ray data were collected at room temperature using an Enraf-Nonius CAD4 diffractometer (graphite-monochromated Cu$K\alpha$ radiation ($\lambda = 1.5418$ Å)). The crystallographic data are summarized in Table 3. The unit cell was

TABLE 3
Crystallographic Data for $[NH_3(CH_2)_2NH_3]_4[Ga_{4x}V_x(HPO_4)_5(PO_4)_3H(OH)_2]$ ($x = 1.65$)

Formula	$[NH_3(CH_2)_2NH_3]_4$ $[Ga_{2.35}V_{1.65}(HPO_4)_5(PO_4)_3H(OH)_2]$
M_r	1296.22
Crystal size (mm)	0.03 × 0.2 × 0.3
Crystal habit	Dark-green plate
Crystal system	Triclinic
Space group	$P-1$
a (Å)	9.991(1)
b (Å)	12.367(1)
c (Å)	15.082(1)
α (°)	90.751(6)
β (°)	91.720(7)
γ (°)	91.449(8)
Cell volume (Å^3)	1861.78
Z	2
Temperature (K)	293
ρ_{calc} (g cm^{-3})	2.31
$\mu_{CuK\alpha}$ (cm^{-1})	98.6
Unique data	7052
Observed data ($I > 3\sigma(I)$)	5985
R_{merge}	0.0248
Residual electron density (min, max) (e Å^{-3})	− 1.27, 0.99
Number of parameters refined	585
R	0.0393
R_w	0.0477

TABLE 4

Fractional Atomic Coordinates, Isotropic Thermal Parameters (Å^2), and Site Occupancies for $[NH_3(CH_2)_2NH_3]_4[Ga_{4-x}V_x(HPO_4)_5(PO_4)_3H(OH)_2]$ ($x = 1.65$)

Atom	x	y	z	U(iso)	Occ[a]
Ga(1)	0.47716(4)	0.39438(3)	0.94618(3)	0.0135	0.823(9)
Ga(2)	0.33626(4)	0.64081(4)	0.83926(3)	0.0123	0.374(9)
Ga(3)	0.98685(4)	1.10142(3)	0.55839(3)	0.0130	0.760(9)
Ga(4)	0.83716(4)	0.85062(4)	0.65276(3)	0.0124	0.395(8)
V(1)	0.47716(4)	0.39438(3)	0.94618(3)	0.0135	0.177(9)
V(2)	0.33626(4)	0.64081(4)	0.83926(3)	0.0123	0.626(9)
V(3)	0.98685(4)	1.10142(3)	0.55839(3)	0.0130	0.240(9)
V(4)	0.83716(4)	0.85062(4)	0.65276(3)	0.0124	0.605(8)
P(1)	0.11892(8)	0.81619(7)	0.75877(6)	0.0173	
P(2)	0.61945(8)	0.67235(7)	0.73928(6)	0.0159	
P(3)	0.38091(8)	0.40834(7)	0.74059(6)	0.0176	
P(4)	0.76843(8)	0.47760(6)	0.99880(5)	0.0143	
P(5)	0.54003(8)	0.16736(6)	1.03149(6)	0.0158	
P(6)	0.89303(9)	1.08157(7)	0.75995(6)	0.0179	
P(7)	0.72875(8)	0.97639(7)	0.49503(5)	0.0154	
P(8)	0.9376(1)	0.66686(7)	0.51614(7)	0.0211	
O(1)	0.4480(3)	0.3595(2)	0.8218(2)	0.0234	
O(2)	0.4614(3)	0.2447(2)	0.9726(2)	0.0219	
O(3)	0.6736(2)	0.4088(2)	0.9372(2)	0.0182	
O(4)	0.2914(2)	0.4137(2)	0.9777(2)	0.0186	
O(5)	0.4800(2)	0.5601(2)	0.9201(2)	0.0158	
O(6)	0.3106(2)	0.5130(2)	0.7590(2)	0.0229	
O(7)	0.1981(2)	0.5856(2)	0.9171(2)	0.0187	
O(8)	0.3575(2)	0.7713(2)	0.9096(2)	0.0225	
O(9)	0.1894(2)	0.7094(2)	0.7716(2)	0.0219	
O(10)	0.4735(2)	0.6961(2)	0.7591(2)	0.0238	
O(11)	0.9732(3)	1.1259(2)	0.6831(2)	0.0220	
O(12)	0.9775(3)	1.2539(2)	0.5355(2)	0.0226	
O(13)	0.7976(2)	1.0846(2)	0.5222(2)	0.0206	
O(14)	1.1846(2)	1.0900(2)	0.5674(2)	0.0197	
O(15)	0.9812(2)	0.9348(2)	0.5762(2)	0.0152	
O(16)	0.8212(3)	0.9743(2)	0.7355(2)	0.0221	
O(17)	0.6961(2)	0.9099(2)	0.5768(2)	0.0193	
O(18)	0.8384(3)	0.7240(2)	0.5728(2)	0.0229	
O(19)	− 0.0255(3)	0.7873(2)	0.7266(2)	0.0259	
O(20)	0.6908(2)	0.7772(2)	0.7184(2)	0.0191	
O(21)	0.1085(3)	0.8808(2)	0.8471(2)	0.0314	
O(22)	0.1898(3)	0.8849(2)	0.6906(2)	0.0237	
O(23)	0.6884(3)	0.6103(2)	0.8124(2)	0.0254	
O(24)	0.6139(3)	0.6000(2)	0.6513(2)	0.0280	
O(25)	0.4821(3)	0.4201(2)	0.6669(2)	0.0247	
O(26)	0.2715(3)	0.3219(2)	0.7056(2)	0.0270	
O(27)	0.8996(2)	0.4966(2)	0.9497(2)	0.0202	
O(28)	0.4440(3)	0.0962(2)	1.0825(2)	0.0230	
O(29)	0.6272(3)	0.0943(2)	0.9716(2)	0.0260	
O(30)	0.8009(3)	1.1640(2)	0.7971(2)	0.0277	
O(31)	0.9981(3)	1.0594(2)	0.8379(2)	0.0284	
O(32)	0.5944(2)	0.9970(2)	0.4462(2)	0.0218	
O(33)	1.0293(3)	0.5932(2)	0.5715(2)	0.0349	
O(34)	0.8533(4)	0.5939(3)	0.4477(2)	0.0354	
N(1)	0.2602(3)	0.6335(3)	0.2434(2)	0.0290	
N(2)	0.0347(4)	0.4419(3)	0.2264(3)	0.0331	
N(3)	0.1142(3)	0.7961(3)	0.0139(2)	0.0296	
N(4)	− 0.1943(4)	0.8030(3)	− 0.0947(3)	0.0353	
N(5)	0.4997(5)	1.0488(5)	0.2693(3)	0.0435	
N(6)	0.7493(3)	0.9065(3)	0.2502(2)	0.0299	
N(7)	0.2811(5)	0.7019(4)	0.5959(3)	0.0493	
N(8)	0.5831(4)	0.7043(3)	0.4856(2)	0.0351	
C(1)	0.1516(4)	0.5975(3)	0.3026(3)	0.0296	
C(2)	0.0277(4)	0.5570(4)	0.2530(3)	0.0338	
C(3)	− 0.0231(4)	0.7483(3)	0.0181(3)	0.0350	
C(4)	− 0.1314(4)	0.8254(4)	− 0.0067(3)	0.0334	
C(5)	0.5049(4)	0.9333(5)	0.2421(3)	0.0391	
C(6)	0.6287(4)	0.9101(3)	0.1915(3)	0.0294	
C(7)	0.3454(5)	0.6755(5)	0.5150(4)	0.0467	
C(8)	0.4556(5)	0.7543(5)	0.4987(5)	0.0513	
H(5)	0.558(5)	0.582(5)	0.888(3)	0.05	
H(15)	1.056(5)	0.920(5)	0.610(3)	0.05	
H(24)	0.563(5)	0.530(4)	0.661(4)	0.05	
H(26)	0.215(5)	0.348(4)	0.655(3)	0.05	
H(27)	1.0	0.5	1.0	0.05	
H(29)	0.585(5)	0.027(4)	0.956(4)	0.05	
H(31)	1.038(5)	0.987(4)	0.842(4)	0.05	
H(32)	0.5	1.0	0.5	0.05	
H(34)	0.878(6)	0.513(3)	0.441(4)	0.05	

[a] Occupancy is 1.00 unless stated otherwise.

determined as triclinic from 24 well-centered reflections and the cell parameters optimized by least-squares refinement ($a = 9.991(1)$, $b = 12.367(1)$, and $c = 15.082(1)$ Å; $\alpha = 90.751(6)$, $\beta = 91.720(7)$, and $\gamma = 91.449(8)°$). Intensity data were then collected over the angle range ($0 \le \theta \le 74.33°$ using the ω–2θ scan technique. Three standard reflections were measured every hour during the data collection and no significant intensity variations were observed. Data were corrected for absorption using ψ-scans and further corrected for Lorentz and polarization effects within the program RC93 (22).

The structure was solved in space group $P-1$ (No. 2 (23)) by direct methods using the program SHELXS (24) and all nonhydrogen framework atoms were located. All subsequent Fourier calculations and least-squares refinements were carried out using the CRYSTALS suite of programs (25). The carbon and nitrogen atoms of the template and framework hydrogen atoms were located in difference Fourier maps. Hydrogen atoms of the template were placed geometrically. It was possible to refine Ga and V site occupancies. The total occupancy at each site was constrained to be unity.

In the final cycle, 585 parameters, including anisotropic thermal parameters for all nonhydrogen framework and template atoms, and positional parameters for the framework hydrogen atoms, were refined. The data were corrected for extinction by the method of Larsen (26) and a three-term Chebyshev polynomial was applied as weighting scheme (27). The refinement converged to give $R = 0.039$ ($R_w = 0.048$).

TABLE 5
Selected Bond Distances (Å) and Angles (°) for $[NH_3(CH_2)_2NH_3]_4[Ga_{4-x}V_x(HPO_4)_5(PO_4)_3H(OH)_2]$ ($x = 1.65$)

M(1)–O(1)	1.931(3)	*M*(3)–O(11)	1.910(2)
M(1)–O(2)	1.901(2)	*M*(3)–O(12)	1.925(3)
M(1)–O(3)	1.975(2)	*M*(3)–O(13)	1.957(2)
M(1)–O(4)	1.949(2)	*M*(3)–O(14)	1.985(2)
M(1)–O(5)	2.091(2)	*M*(3)–O(15)	2.080(2)
M(1)–O(5)^{a}	2.115(2)	*M*(3)–O(15)^{b}	2.108(2)
M(2)–O(5)	2.132(3)	*M*(4)–O(15)	2.132(2)
M(2)–O(6)	1.985(2)	*M*(4)–O(16)	1.973(2)
M(2)–O(7)	1.954(2)	*M*(4)–O(17)	1.953(3)
M(2)–O(8)	1.923(2)	*M*(4)–O(18)	1.965(2)
M(2)–O(9)	1.977(3)	*M*(4)–O(19)^{c}	1.929(3)
M(2)–O(10)	1.971(2)	*M*(4)–O(20)	1.996(2)
P(1)–O(9)	1.525(3)	P(2)–O(10)	1.532(3)
P(1)–O(19)	1.540(3)	P(2)–O(20)	1.506(2)
P(1)–O(21)	1.552(3)	P(2)–O(23)	1.510(3)
P(1)–O(22)	1.523(2)	P(2)–O(24)	1.590(3)
P(3)–O(1)	1.518(3)	P(6)–O(11)	1.528(2)
P(3)–O(6)	1.515(3)	P(6)–O(16)	1.528(2)
P(3)–O(25)	1.531(2)	P(6)–O(30)	1.504(3)
P(3)–O(26)	1.583(3)	P(6)–O(31)	1.583(3)
P(4)–O(3)	1.540(2)	P(7)–O(13)	1.534(2)
P(4)–O(4)^{a}	1.527(2)	P(7)–O(14)^{b}	1.541(2)
P(4)–O(7)^{a}	1.532(3)	P(7)–O(17)	1.530(2)
P(4)–O(27)	1.539(2)	P(7)–O(32)	1.540(3)
P(5)–O(2)	1.530(3)	P(8)–O(12)^{b}	1.518(2)
P(5)–O(8)^{a}	1.517(2)	P(8)–O(18)	1.510(2)
P(5)–O(28)	1.518(2)	P(8)–O(33)	1.543(4)
P(5)–O(29)	1.568(3)	P(8)–O(34)	1.572(3)
O(5)–H(5)	0.96(4)	O(29)–H(29)	0.94(4)
O(15)–H(15)	0.91(4)	O(31)–H(31)	0.99(4)
O(24)–H(24)	1.01(4)	O(32)–H(32)	1.264(2)
O(26)–H(26)	0.99(4)	O(34)–H(34)	1.04(4)
O(27)–H(27)	1.239(2)		
O(1)–*M*(1)–O(2)	89.5(1)	O(11)–*M*(3)–O(12)	91.6(1)
O(1)–*M*(1)–O(3)	93.9(1)	O(11)–*M*(3)–O(13)	100.9(1)
O(2)–*M*(1)–O(3)	99.7(1)	O(12)–*M*(3)–O(13)	89.2(1)
O(1)–*M*(1)–O(4)	98.6(1)	O(11)–*M*(3)O(14)	92.7(1)
O(2)–*M*(1)–O(4)	90.2(1)	O(12)–*M*(3)–O(14)	98.6(1)
O(3)–*M*(1)–O(4)	164.18(9)	O(13)–*M*(3)–O(14)	164.1(1)
O(1)–*M*(1)–O(5)	91.3(1)	O(11)–*M*(3)–O(15)	90.9(1)
O(2)–*M*(1)–O(5)	175.8(1)	O(12)–*M*(3)–O(15)	174.9(1)
O(3)–*M*(1)–O(5)	84.40(9)	O(13)–*M*(3)–O(15)	85.9(1)
O(4)–*M*(1)–O(5)	85.64(9)	O(14)–*M*(3)–O(15)	85.75(9)
O(1)–*M*(1)–O(5)^{a}	176.0(1)	O(11)–*M*(3)–O(15)^{b}	174.3(1)
O(2)–*M*(1)–O(5)^{a}	93.4(1)	O(12)–*M*(3)–O(15)^{b}	92.0(1)
O(3)–*M*(1)–O(5)^{a}	82.92(9)	O(13)- *M*(3)–O(15)^{b}	83.63(9)
O(4)–*M*(1)–O(5)^{a}	84.16(9)	O(14)–*M*(3)–O(15)^{b}	82.32(9)
O(5)–*M*(1)–O(5)^{a}	86.1(1)	O(15)–*M*(3) -O(15)^{b}	85.84(9)
O(5)–*M*(2)–O(6)	92.0(1)	O(15)–*M*(4)–O(16)	92.49(9)
O(5)–*M*(2)–O(7)	87.99(9)	O(15)–*M*(4)–O(17)	88.67(9)
O(6)–*M*(2)–O(7)	91.1(1)	O(16)–*M*(4)–O(17)	89.5(1)
O(5)–*M*(2)–O(8)	91.8(1)	O(15)–*M*(4)–O(18)	91.63(9)
O(6)–*M*(2)–O(8)	175.7(1)	O(16)–*M*(4)–O(18)	175.4(1)
O(7)–*M*(2)–O(8)	91.0(1)	O(17)–*M*(4)–O(18)	88.5(1)
O(5)–*M*(2)–O(9)	174.40(9)	O(15)–*M*(4)–O(19)^{c}	92.3(1)
O(6)–*M*(2)–O(9)	87.8(1)	O(16)–*M*(4)–O(19)^{c}	92.1(1)
O(7)–*M*(2)–O(9)	86.4(1)	O(17)–*M*(4)–O(19)^{c}	178.1(1)
O(8)–*M*(2)–O(9)	88.6(1)	O(18)–*M*(4)–O(19)^{c}	89.8(1)
O(5)–*M*(2)–O(10)	92.8(1)	O(15)–*M*(4)–O(20)	175.4(1)
O(6)–*M*(2)–O(10)	88.3(1)	O(16)–*M*(4)–O(20)	87.3(1)
O(7)–*M*(2)–O(10)	179.0(1)	O(17)–*M*(4)–O(20)	86.7(1)
O(8)–*M*(2)–O(10)	89.5(1)	O(18)–*M*(4)–O(20)	88.5(1)
O(9)–*M*(2)–O(10)	92.8(1)	O(19)^{c}–*M*(4)–O(20)	92.4(1)
M(1)–O(5)–*M*(1)^{a}	93.9(1)	*M*(3)–O(15)–*M*(3)^{b}	94.16(9)
M(1)–O(5)–*M*(2)	125.4(1)	*M*(3)- O(15)–*M*(4)	124.4(1)
M(1)^{a}–O(5)–*M*(2)	122.4(1)	*M*(3)^{b}–O(15)–*M*(4)	123.2(1)
M(1)–O(1)–P(3)	138.3(2)	*M*(3)–O(11)–P(6)	138.5(1)
M(1)–O(2)–P(5)	134.9(2)	*M*(3)–O(12)–P(8)^{b}	134.0(2)
M(1)–O(3)–P(4)	126.0(1)	*M*(3)–O(13)–P(7)	124.2(1)
M(1)–O(4)–P(4)^{a}	124.5(1)	*M*(3)–O(14)–P(7)^{b}	125.9(1)
M(1)–O(5)–H(5)	112.0(34)	*M*(3)–O(15)–H(15)	106.0(37)
M(1)^{a}–O(5)–H(5)	105.9(34)	*M*(3)^{b}–O(15)–H(15)	110.1(36)
M(2)–O(6)–P(3)	137.5(2)	*M*(4)–O(16)–P(6)	139.6(1)
M(2)–O(7)–P(4)^{a}	122.4(1)	*M*(4)–O(17)–P(7)	121.5(1)
M(2)–O(8)–P(5)^{a}	141.1(2)	*M*(4)–O(18)–P(8)	137.7(2)
M(2)–O(9)–P(1)	142.9(2)	*M*(4)^{d}–O(19)–P(1)	137.4(2)
M(2)–O(10)–P(2)	137.0(2)	*M*(4)–O(20)–P(2)	147.1(2)
O(27)–H(27)–O(27)^{e}	180	O(32)–H(32)–O(32)^{f}	180

Note. M sites contain both Ga and V. N–C and C–C bond lengths lie in the ranges 1.433(6) to 1.484(8) and 1.481(8) to 1.504(6) Å, respectively. O–P–O angles in PO_4 tetrahedra lie in the range 103.8(1) to 114.3(1)°. Symmetry transformations used to generate equivalent atoms: $^{a}1-x, 1-y, 2-z$; $^{b}2-x, 2-y, 1-z$; $^{c}1+x, y, z$; $^{d}-x, y, z$, $^{e}2-x, 1-y, 2-z$; $^{f}1-x, 2-y, 1-z$.

Fractional atomic coordinates and isotropic thermal parameters are given in Table 4 and selected bond distances and angles in Table 5. The local coordination of the framework atoms is shown in Fig. 1.

RESULTS AND DISCUSSION

The structure consists of layers of formula $[Ga_{2.35}V_{1.65}(HPO_4)_5(PO_4)_3H(OH)_2]^{8-}$ lying parallel to the (011) plane between which lie ethylenediamine dications $[NH_3(CH_2)_2NH_3]^{2+}$ for charge balancing. The VGaPO layers contain four crystallographically distinct *M* atoms (where *M* is a statistical mixture of V^{3+} and Ga^{3+}) and eight P atoms present in octahedral MO_6 and tetrahedral PO_4 units, respectively. Bond-valence calculations (30) support the assignments of the metal and phosphorus sites as trivalent and pentavalent, respectively. The MO_6 polyhedra link to form two M_4O_{20} tetramers which in turn act as

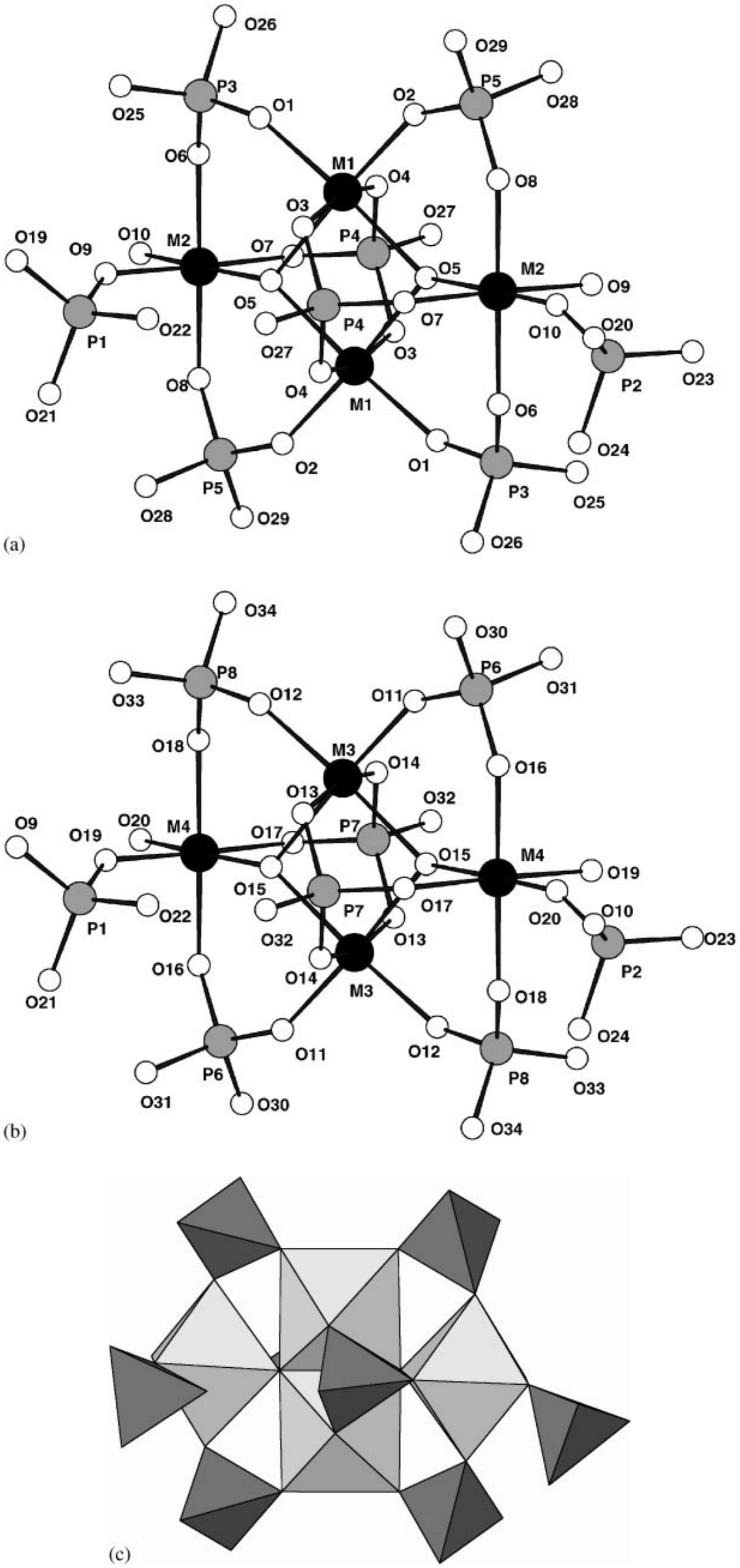

FIG. 1. (a and b) Ball-and-stick representations of the local coordination and numbering schemes of the two distinct tetrameric metal-based clusters in the title compound. Hydrogen atoms have been omitted. (Drawing package, CAMERON (28).) (c) Polyhedral representation of either cluster. Key: MO_6 octahedra (M = Ga, V), pale gray; PO_4 tetrahedra, dark gray. (Drawing package, ATOMS (29)).

"secondary building units" (Fig. 1). The first tetramer consists of a central pair of edge-sharing $M(1)O_6$ octahedra connected *via* two oxygens (O(5)) to which two additional $M(2)O_6$ octahedra are attached by corner sharing also *via* O(5). Similar sharing is also involved in the second tetramer in which edge-sharing $M(3)O_6$ octahedra are linked through O(15) to $M(4)O_6$. Difference Fourier maps suggest that O(5) and O(15) are protonated. The MO_6 polyhedra have far from regular octahedral geometry, the distortion being greater in the $M(1)O_6$ and $M(3)O_6$ edge-sharing units as observed previously in similar tetrameric units (15). The refined occupancies of the metal sites indicate that vanadium preferentially occupies the corner-sharing octahedra $M(2)O_6$ and $M(4)O_6$.

While oxygen atoms O(5) and O(15) bridge three metal centers in their respective tetramers, the remaining oxygens each bond to a phosphorus atom in one of the eight crystallographically distinct PO_4 groups. Four of the PO_4 groups, $P(3)O_4$, $P(5)O_4$, $P(6)O_4$, and $P(8)O_4$, have bonds to two adjacent metal atoms within the same tetramer. Of the remaining P–O bond lengths, one per PO_4 group is significantly longer than the others (P(3)–O(26), 1.583(3); P(5)–O(29), 1.568(3); P(6)–O(31), 1.583(3); and P(8)–O(34), 1.572 Å), implying the presence of P–OH groups. This assignment was confirmed by the location of hydrogen atoms at $\sim$ 1 Å from oxygens O(26), O(29), O(31), and O(34) in the difference Fourier maps. The fourth oxygen of each PO_4 unit (O(25), O(28), O(30), and O(33)) is bonded only to the corresponding phosphorus, suggesting some multiple bond character although the P–O bond lengths are not particularly short (P–O distances in the range 1.504(3)–1.543(4) Å) partly as a result of the interlayer and layer–diamine hydrogen bonding interactions discussed below. Two of the remaining PO_4 groups, $P(4)O_4$ and $P(7)O_4$, both have bonds to three adjacent metal atoms within the same M_4O_{20} unit. The fourth oxygen of each unit, O(27) and O(32), associated with P(4) and P(7), respectively, is involved in intralayer hydrogen bonding. The remaining PO_4 groups, $P(1)O_4$ and $P(2)O_4$, serve to link the two distinct tetramers together via oxygens O(9) and O(19) for P(1) and O(10) and O(20) for P(2), to generate the layer structure (Fig. 2). O(24) forms part of a hydroxyl group (P(2)–O(24), 1.590(3) Å) and again hydrogen bonding interactions can account for the elongation to a greater or lesser extent of the remaining terminal P–O bonds in the $P(1)O_4$ and $P(2)O_4$ polyhedra (P(1)–O(21), 1.552(3), P(1)–O(22), 1.523(2); P(2)–O(23), 1.510(3) Å). Terminal P = O groups in, for example, $H_3PO_4.0.5H_2O$ are 1.485 and 1.495 Å in length (31).

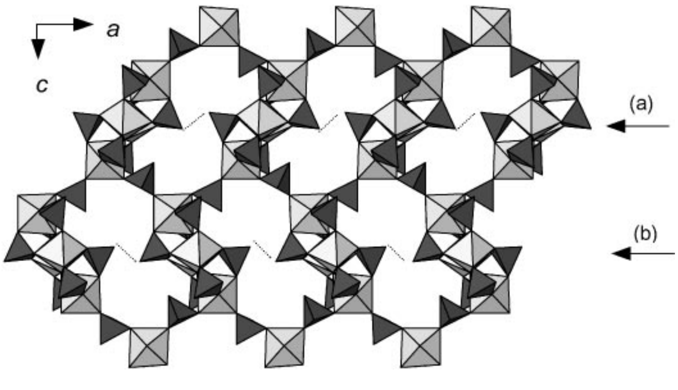

FIG. 2. View along the *b* axis of a VGaPO layer. There are two series of crystallographically distinct windows which lie in alternate stripes indicated by arrows (a) and (b). The short O ... O cross-window distances (2.527(5) and 2.478(5) Å in windows along (a) and (b), respectively) are represented by dotted lines. The framework hydrogen atoms and ethylenediamine cations have been omitted. Key as for Fig. 1c. (Drawing package, ATOMS (29)).

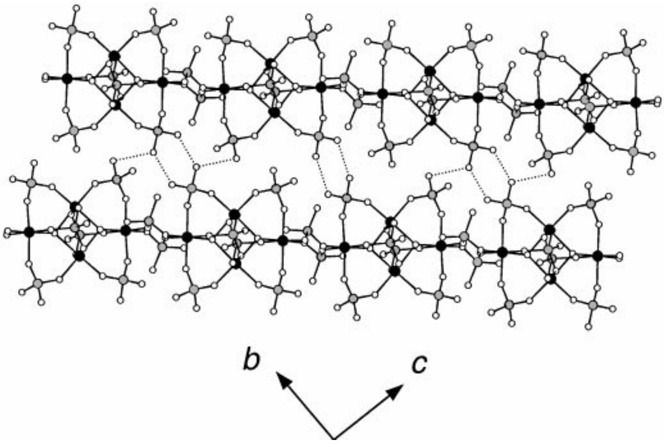

FIG. 3. View along the *a* axis showing the hydrogen bonding interactions between adjacent VGaPO layers. O ... O distances in the range 2.559(3)–2.819(5) Å are represented by dotted lines. Ethylenediamine cations and framework hydrogen atoms are not shown. Key as for Fig. 1a. (Drawing package, CAMERON (28)).

Within the layers are two sets of "bow tie"-shaped windows which, although crystallographically distinct, have similar geometries (long axes O(22) ... O(22), 9.013(5) and O(23) ... O(23), 8.798(6) Å; short axes O(27) ... O(27), 2.478(5) and O(32) ... O(32), 2.527(5) Å). Hydrogen atoms were located midway between the pairs of O(27) and O(32) atoms in the two sets of windows, implying the presence of strong symmetrical hydrogen bonds. There are a number of additional short OH ... O distances within the layers leading to a complicated network of intralayer hydrogen bonds (O(5)H ... O(23), 2.743(3); O(13) ... O(15)H, 2.713(3); O(15)H ... O(22), 2.752(3); O(21) ... O(31)H, 2.498(4); O(24)H ... O(25), 2.572(4) Å)). Adjacent layers are connected by strong hydrogen bonds (O(26)H ... O(34), 2.819(5); O(28) ... O(29)H, 2.559(3); and O(33) ... O(34)H, 2.631(4) Å) which serve to hold the structure together (Fig. 3). The layers stack so that the windows are aligned to produce channels running through the structure parallel to the

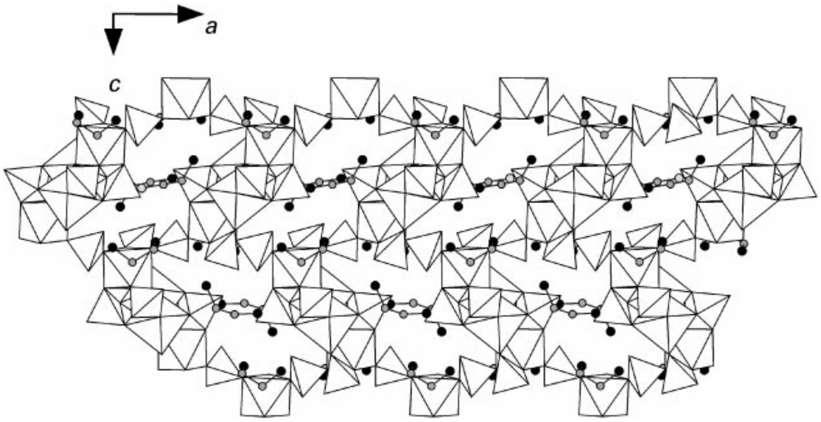

FIG. 4. View along the *b* axis showing the location of the ethylenediamine dications relative to the VGaPO layer. Key: N atoms, black; C atoms, light gray. (Drawing package, ATOMS (29)).

b axis. Four crystallographically distinct ethylenediamine cations are located in the interlayer voids, two of which lie within the channels (Fig. 4). One nitrogen of each molecule is involved in hydrogen bonding to framework oxygens of one layer only (N(2), N(4), N(5), and N(7) ... O distances in the range 2.827(4)–3.080(6) Å) while the other bonds to oxygens in both adjacent layers (N(1), N(3), N(6), N(8) ... O distances in the range 2.668(5)–3.104(4) Å).

CONCLUSIONS

The title compound, $[NH_3(CH_2)_2NH_3]_4$ $[Ga_{4-x}V_x(HPO_4)_5(PO_4)_3H(OH)_2]$ ($x = 1.65$), is the third example of an organically templated vanadium–gallium phosphate to be characterized and the first *Me*GaPO described possessing a layered structure. The structure has high pseudosymmetry. The two tetrameric units, and in turn the two types of windows generated within the layers, although crystallographically distinct, possess very similar geometries. The actual low symmetry of the crystal, however, derives mainly from the positions of the template molecules.

The M_4O_{20} tetrameric units found in the layers have previously been identified in a number of other phases including the isostructural series $[NH_3(CH_2)_zNH_3]_2$ $[M_4(HPO_4)_2(PO_4)_3(OH)_3].yH_2O$ (when $z = 3$, $M = Ga$ (32) or Fe (32); when $z = 4$, $M = Ga$ (15) or mixed (V, Ga) (15) or In (32)) and a second group of phases $NH_4[Ga_2(PO_4)_2(OH)(H_2O)].H_2O$ (33), AlPO-15 (34)), $GaPO_4.2H_2O$ (35), and $GaPO_4$-C_7 (36), all of which have structures closely related to that of the mineral leucophosphite, $K[Fe_2(PO_4)_2(OH)(H_2O)].H_2O$ (37, 38). All these materials have three-dimensional framework structures. In the latter series, the tetramers are linked solely by PO_4 groups, whereas in the latter, both P–O–*M* and *M*–OH–*M* bridges are involved in generating a more open 3-D framework structure. A further phase, $[C_4N_2H_{12}]_{1.5}[Fe_2(H_2PO_4)(HPO_4)_2(PO_4)(OH)].0.5H_2O$ (32, 39), also contains Fe_4O_{20} units. In this structure, the tetramers are linked via PO_4 groups in one direction only to form chains. Terminal $O=PO(OH)_2$ and $O=PO_2(OH)$ groups preclude linking of neighboring chains. Similar behavior is observed in the title compound where the layers are also terminated by $O=PO_2(OH)$ groups.

Given the occurrence of Ga_4O_{20} tetramers in many of the above materials, it is not unreasonable to assume that it should be possible to prepare a gallium-only analogue of the title compound. Such phases are currently being investigated.

ACKNOWLEDGMENTS

The authors thank K. J. Peacock for assistance with preliminary synthetic investigations. In addition, A.M.C. thanks The University of Reading Endowment Trust Fund for financial assistance and A.R.C. thanks the EPSRC for a research studentship.

REFERENCES

1. A. K. Cheetham, G. Férey, and T. Loiseau, *Angew. Chem. Int. Ed.* **38,** 3268 (1999).
2. A. M. Chippindale and A. R. Cowley, *Microporous Mesoporous Mater.* **21,** 271 (1998).
3. A. M. Chippindale and R. I. Walton, *J. Chem. Soc. Chem. Commun.* 2453 (1994).
4. A. D. Bond, A. M. Chippindale, A. R. Cowley, J. E. Readman, and A. V. Powell, *Zeolites* **19,** 326 (1997).
5. A. R. Cowley and A. M. Chippindale, *Chem. Commun.* 673 (1996).
6. A. M. Chippindale, A. R. Cowley, and K. J. Peacock, *Microporous Mesoporous Mater.* **24,** 133 (1998).
7. X. Bu, T. E. Gier, P. Feng, and G. Stucky, *Microporous Mesoporous Mater.* **20,** 371 (1998).
8. A. M. Chippindale and A. R. Cowley, *Zeolites* **18,** 176 (1997).
9. A. R. Cowley and A. M. Chippindale, *Microporous Mesoporous Mater.* **28,** 163 (1999).
10. X. Bu, P. Feng, and G. Stucky, *Science* **278,** 2080 (1997).

11. A. M. Chippindale, A. R. Cowley, and A. D. Bond, *Acta Crystallogr. C* **54,** 1 (1998).
12. A. R. Overweg, J. W. de Haan, P. C. M. M. Magusin, R. A. van Santen, G. Sankar, and J. M. Thomas, *Chem. Mater.* **11,** 1680 (1999).
13. A. M. Chippindale, A. D. Bond, A. R. Cowley, and A. V. Powell, *Chem. Mater.* **9,** 2380 (1997).
14. K. F. Hsu and S.L. Wang, *Chem. Commun.* 135 (2000).
15. A. M. Chippindale, K. J. Peacock, and A. R. Cowley, *J. Solid State Chem.* **145,** 379 (1999).
16. A. M. Chippindale, *Chem. Mater.* **12,** 818 (2000).
17. R. P. Hammond and J. A. Zubieta, *J. Solid State Chem.* **144,** 442 (1999).
18. Q. Kan, F. Glasser, and R. Xu, *J. Mater. Chem.* **3,** 983 (1993).
19. JCPDS Powder Diffraction File No. 8-497, JCPDS International Center for Diffraction Data, Swathmore, PA, 1987.
20. J. W. Johnson, A. J. Jacobson, J. F. Brody, and S. M. Rich, *Inorg. Chem.* **21,** 3820 (1982).
21. A. M. Chippindale, unpublished results.
22. D. J. Watkin, C. K. Prout, and P. M. deQ. Lilley, RC93 User Guide, Chemical Crystallography Laboratory, University of Oxford, U.K., 1994.
23. "International Tables for Crystallography, Volume A" (T. Hahn, Ed.), Kluwer Academic Publishers, Dordrecht, 1995.
24. G. M. Sheldrick, SHELX-86 Program for Crystal Structure Determination, University of Cambridge, 1986.
25. D. J. Watkin, C. K. Prout, J. R. Carruthers, and P. W. Betteridge, CRYSTALS, issue 10, Chemical Crystallography Laboratory, University of Oxford, U.K. 1994.
26. A. C. Larsen, *Acta Crystallogr.* **23,** 664 (1967).
27. J. R. Carruthers and D. J. Watkin, *Acta Crystallogr. A* **35,** 698 (1979).
28. L. J. Pearce, C. K. Prout, and D. J. Watkin, CAMERON User Guide, Chemical Crystallography Laboratory, University of Oxford, Oxford, U.K., 1993.
29. ATOMS for Windows v. 4.0, Shape Software, 521 Hidden Valley Rd., Kingsport, TN 37663.
30. N. E. Brese and M. O'Keefe, *Acta Crystallogr. B* **47,** 192 (1991).
31. B. Dickens, E. Prince, L. W. Schroeder, and T. H. Jordan, *Acta Crystallogr. B* **30,** 1470 (1974).
32. K. H. Lii, Y. F. Huang, V. Zima, C. Y. Huang, H. M. Lin, Y. C. Jiang, F. L. Liao, and S. L. Wang, *Chem. Mater.* **10,** 2599 (1998).
33. T. Loiseau and G. Férey, *Eur. J. Solid State Inorg. Chem.* **31,** 575 (1994).
34. J. J. Pluth, J. V. Smith, J. M. Bennett, and J. P. Cohen, *Acta Crystallogr. C* **40,** 2008 (1984).
35. R. C. L. Mooney-Slater, *Acta Crystallogr.* **20,** 526 (1966).
36. W. Tieli, Y. Guangdi, F. Shouhua, S. Changjiang, and R. Xu, *J. Chem. Soc., Chem. Commun.* 948 (1989).
37. P. B. Moore, *Am. Mineral.* **57,** 397 (1972).
38. S. Dick and T. Zeiske, *J. Solid State Chem.* **133,** 508 (1997).
39. V. Zima and K. H. Lii, *Dalton Trans.* 4109 (1998).